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ELECTRON PARAMAGNETIC RESONANCE INVESTIGATION OF FOREIGN RADICAL IONS IN IRRADIATED STRONTIUM AND ZINC ACETATE SINGLE CRYSTALS

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THESIS

ELECTRON PARAMAGNETIC RESONANCE INVESTIGATION OF FOREIGN RADICAL IONS IN IRRADIATED STRONTIUM AND ZINC ACETATE SINGLE CRYSTALS

by

William Edward Oney, Jr.

Thesis Advisor: William M. Tolles

June 1971

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Electron Paramagnetic Resonance Investigation
# of Foreign Radical Ions in Irradiated
Strontium and Zinc Acetate Single Crystals

by

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Submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE IN PHYSICS

from the

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June 1971

ABSTRACT

An EPR study of x-ray irradiated isobutyrate and n-butyrate doped strontium acetate hemihydrate has been made. The n-butyrate radical exhibited anistropy while the isobutyrate did not. The n-butyrate radical ion has a spectrum of 8 lines of equal intensity. The unpaired electron is on the α carbon and the two β carbon hydrogens are inequalivalent. The n-butyrate radical has been shown to be oriented in very nearly the same position as the propionate radical previously reported and it occupies only one of the two acetate sites. Within this site only one rotamer of the damaged ion is thermally populated. The isobutyrate ion is selectively damaged by a ratio of 300 to 1, and the ratio for n-butyrate is about 500 to 1.

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I. INTRODUCTION

The study of radical fragments resulting from radiation damage in sodium, cupric, nickel, zinc and strontium acetates has been reported [1]. Coneway [2] has recently reported on lithium and mercuric acetates. In most cases the work emphasized reactions involving the acetate ion at various temperatures. However, Tolles, Sanders and Gisch [1] found that in the presence of trace amounts of propionate ion, in both zinc and strontium acetates, the damage was preferentially transferred to the propionate ion and yields $CH_3\dot{C}HCO_2^{-}$ as a major product. In strontium acetate this preference is 700 to 1 while in zinc acetate it is 20 to 1.

It is the purpose of this thesis to provide additional data on the effects of other trace impurities in strontium and zinc acetate single crystals. This additional data will, hopefully, provide some new insight into the mechanism by which the damage moves through the crystal lattice. The other trace impurities studied were isobutyrate and n-butyrate. The results of this investigation would also give information on the value of zinc and strontium acetates as host crystals for the introduction of materials for study by EPR. Another purpose was to provide additional information on the structure of strontium acetate crystals.

II. EPR THEORY

EPR theory has been well elucidated by many authors, most notable Carrington and McLachlan [3] in their book on magnetic resonance. This thesis is particularly concerned with the EPR of trapped organic radicals and the discussion herein will be limited to only that portion of the subject.

The study of trapped organic radicals in single crystals is useful because the radicals induced in them are regularly oriented with respect to the crystal axis, and therefore to the external magnetic field. This regular orientation of these radicals allows the measurement of anisotropic hyperfine magnetic interaction.

The problem here is to find the parameters in the spin Hamiltonian for the interaction of an unpaired electron with one or more nuclei. The spin Hamiltonian is

$$\mathcal{H} = \beta \vec{H}\cdot\overset{\rightrightarrows}{g}\cdot\vec{S} - \sum_i \gamma_i \hbar \vec{H}\cdot\vec{I}_i + \sum_i \vec{S}\cdot\overset{\rightrightarrows}{T}\cdot\vec{I}_i$$

where β is the Bohr magneton, H is the external field, g is the spectroscopic splitting tensor, γ_i the nuclear magneton, T is hyperfine interaction tensor, and S and I the electron and nuclear spin respectively. The first term represents the interaction of the electron with the external field. For trapped organic radicals the g tensor is very nearly equal to the free election g value. The second term is the sum of the interactions of the various nuclei with the external field. At X-band frequencies the effect

of this term is small. The third term then represents the heart of the problem: the energy of interaction between the electron spin and the various nuclei.

The hyperfine interaction term is a combination of the isotropic Fermi contact interaction and the anisotropic dipolar interaction. This hyperfine interaction for a single nucleus may be written as:

$$\mathcal{H}' = \vec{S}\cdot\overset{\leftrightarrow}{T}\cdot\vec{I} = \frac{8\pi g\beta\gamma_N\psi^2(0)}{3}\vec{S}\cdot\vec{I} - g\beta\gamma_N\left[\frac{\vec{S}\cdot\vec{I}}{r^3} - \frac{3(\vec{S}\cdot\vec{r})(\vec{I}\cdot\vec{r})}{r^5}\right]$$

The first term is zero unless there is a finite probability of finding the unpaired electron at the interacting nucleus. It is for this reason that it is called the Fermi contact interaction. The second term gives an anisotropic or direction dependent character to hyperfine interaction. The term results from the usual electron and nuclear dipole interaction.

The eigenvalues of H' are the principle values of T. The isotropic components are obtained from the first term in the equation and the anisotropic components from the second term.

In this thesis the interactions studied were the interactions of an electron with hydrogen nucleus or protons. These nuclei have a spin of 1/2. This then will give rise to a spectrum of 2^n equally intense lines if the electron does not see the protons as equivalent. For equivalent protons there are $n + 1$ lines with their relative intensities given by the binomial distribution.

III. BACKGROUND

The literature of EPR spectra of trapped organic radicals is quite extensive [4] . Crystals of organic acids and their salts, when irradiated with x-rays, gamma rays, or high energy electrons, have been found to provide suitable hosts for the resulting trapped radicals. The radical can be identified and its orientation can often be fixed by interpretation of the hyperfine interaction.

Bennet and Gale [5] reported the spectra of polycrystalline carboxylic acid radical anions prepared from formic acid, acetic acid, deuterated acetic acid (d_1 and d_4), propionic acid, butyric acid, trimethylacetic acid and benzoic acid at 77° K. Isobutyric acid failed to give a carboxylic acid radical anion but instead gave the 2-carboxyl 2-propyl radical ($(CH_3)_2\dot{C}COOH$). It was found that the radical anions were able to abstract hydrogen from adjacent neutral molecules at 77° K to give secondary radicals. The extent of the reaction was found to depend on the strength of the C-H bonds in the acid. Negligible reaction occurs with acetic acid which possesses only primary hydrogens, whereas the radical anion reacts completely with the tertiary hydrogen in isobutyric acid.

Detailed studies by McConnell and Heller [6] and others of irradiated dicarboxylic acids, such as malonic and succinic acid, have shown that the ESR lines exhibited by

the radicals arise from the hyperfine interaction of the magnetic moments of the unpaired electron with the magnetic moments of one or more protons in the aliphatic chain. Heller [7] extended this work to methyl malonic acid. Although he identified two species, $CH_3C(COOH)_2$ and $CH_3CHCOOH$, he made a detailed study only of the first. He concluded that the three methyl protons are equivalent, and the principal values of their hyperfine coupling tensor are 75.4 (along the $C-CH_3$ bond), 68.8 and 68.6 MHz, the isotropic component of the coupling tensor (and, therefore, the spin density on the methyl protons) is positive; and that the methyl group executes nearly free rotation about the C-C bond at 4.2^o.

Pooley and Whiffen [8] confirmed and extended the work of McConnell and Heller [6] on a γ irradiated single crystal of succinic acid. They reported the coupling tensors, and the g tensor. These confirmed that the radical has almost the same orientation as the original molecules in the crystal lattice. They found that the plane of the free radical is twisted 5^o from the original carbon skeleton plane and this leads to appreciable non-equivalence of the hydrogen atoms of the CH_2 group.

Morton [9] reported the EPR spectrum of $(CH_3)_2CO_2^-$ trapped in α· aminoisobutyric acid at 40^o C. He concluded that at this temperature, one of the methyl groups was experiencing free rotation, whereas the other was undergoing hindered rotation. Wells and Box [10] extended the investigation by applying ENDOR techniques at 4.2^o K which allowed

the absorption signals for the protons of the two methyl groups to be distinguished at all crystal orientations. The hyperfine tensors for these groups are found to depart from the generally assumed axial symmetry. The nonrotating methyl group permitted an accurate determination of the parameters in the coupling equation $A = B^{o} + B\cos^{2}\theta$. The experimental values found were $B_{o} = 3.2$ MHz and $B = 123.3$ MHz.

Kispert and Rogers [11] reported the interpretation of the EPR Spectrum of single crystals of sodium acetate trihydrate irradiated by 1-MeV electrons at 77° K. They observed four lines with intensity ratios nearly 1:3:3:1 and proton hyperfine splitting of 22.5 G. Each side of these lines had two satellites spaced 5.6 G on either side to form a twelve line pattern. They attributed the quartet to the CH_3 radical and reported the corresponding proton splitting tensor which was axially symmetrical (in the principal axis system) and nearly isotropic. The satellite lines were attributed to "spin-flip" type transitions which arise when there is a simultaneous change in the spin state of the unpaired election of the methyl radical and of neighboring protons. They stated that the neighboring protons giving rise to these transitions were probably those of the water of crystallization.

Tolles, Crawford, and Valenti [12] x-ray irradiated zinc acetate single crystals at 77°C. EPR examination at this temperature revealed an intense 1:3:3:1 quartet with

anisotropic hyperfine coupling constant of 62 MHz. These lines were interpreted to be due to the methyl radical. Examination at 120° - 140° K revealed the decay of the methyl radical and the simultaneous growth of a second species which was shown to $\cdot CH_2CO_2^-$. They proposed that the mechanism was a simple abstraction of a hydrogen atom by the methyl radical from a neighboring acetate ion. Hyperfine and g tensors were calculated and were found to be consistent with a planar $\cdot CH_2CO_2^-$ ion having an HCH bond angle of $116.9^\circ + -0.3^\circ$.

Tolles, Sanders, and Gisch [1] found that x-ray irradiated strontium acetate hemihydrate at room temperature showed a very complex spectrum. After realizing that the complexity was caused by a second spectrum from a trace impurity, they were able to provide an interpretation. They found that $CH_3\dot{C}O_2^{2-}$ was produced rather than the methyl radical as in sodium and zinc acetates. At higher temperatures this spectrum is replaced with two magnetically distinct $\cdot CH_2CO_2^-$ radicals. In the presence of the propionate ion, further reaction proceeds at about $-30^\circ C$ to yield one rotamer of one magnetically distinct $CH_3\dot{C}HCO_2^-$ radical. The ratio of propionate to acetate damage at room temperature was found to be 700:1 in strontium acetate, indicating some mechanism for the delocalization of the damage. This same reaction with a substituted propionate ion occurs in zinc acetate with a ratio of 20:1.

IV. EXPERIMENTAL

A. GROWING OF CRYSTALS

Single crystals of strontium acetate hemihydrate, some with various amounts of strontium n-butyrate added and others with various amounts of strontium isobutyrate added, were grown. They were cultivated by making aqueous solutions of the mixture and allowing slow evaporation from partially covered petri dishes. Crystal quality was improved by adding a small amount of acetic acid. It was found that approximately 20 grams of strontium acetate in 50 ml of solution gave the best results.

It was also found that trace impurities, principally propionate, in commercially available strontium acetate obscured the spectrum obtained. This effect was observed by Tolles et al [1] . In one sample of commercial strontium acetate there was about 0.03% propionate impurity. An effort was made to make purified strontium acetate by reacting strontium oxide with acetic acid selected for its low propionate content. However, analysis revealed that the various batches of available acetic acid contained between 0.01% and 0.03% propionic acid. Distillation of the acetic acid was attempted using a spinning band column with 30 theoretical plates. One batch of acetic acid containing 0.029% propionate had one cut, the best, that had only 0.0032% propionate. Another batch containing

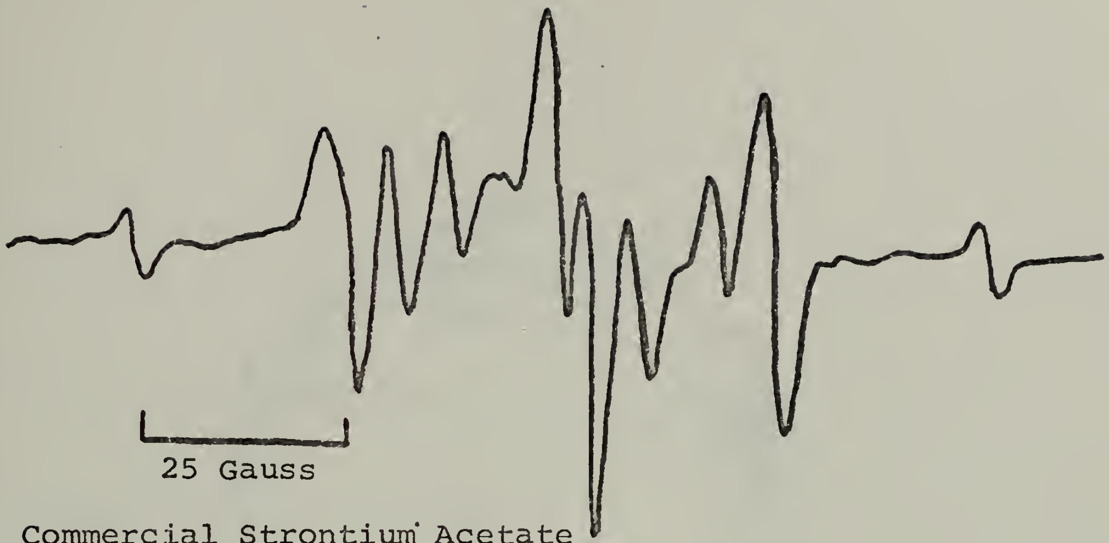
0.13% propionate originally had no measurable amount of propionate in the best cut. All analyses of the acetic acid were made on a Bendix Chroma-Lab series 2200 gas chromatograph with a 10-ftX¼-in OD column packed with 20% FAAP and 70/80 mesh acid washed DMCS and chromsorb W. A flame ionization detector was used.

The spectrum obtained from both commercial strontium acetate and that prepared from distilled acetic acid and strontium oxide is presented in Fig. 1. A much cleaner spectrum results from the purified strontium acetate. The lines in the wings have been identified as belonging to strontium propionate.

An attempt was made to grow zinc acetate crystals doped with zinc isobutyrate and zinc n-butyrate. It was found that the crystals became increasingly fragile and misshaped with increased amounts of doping material. Crystals with a large enough concentration of impurity to give good spectra could not be made.

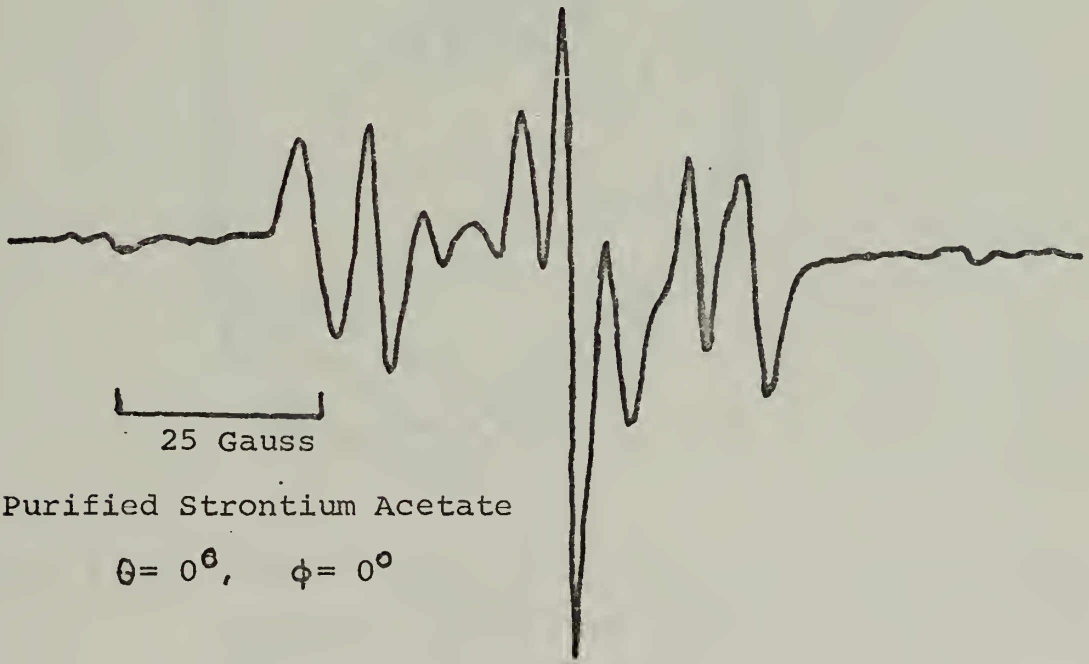
B. CRYSTAL ORIENTATION

The crystal structure of strontium acetate hemihydrate has not, to the knowledge of the author, been reported. The crystal axis system that was used was that reported by Gisch [13] and shown in Fig. 2. The numbers along the edge of the crystal are the angles the crystal faces make with the XY plane. The crystal was positioned on a quartz rod holder with the aid of a microscope. One of the eyepieces had crosshairs to assist in positioning. The orientation



Commercial Strontium Acetate

$\theta = 0^\circ, \ \phi = 0^\circ$



Purified Strontium Acetate

$\theta = 0^\circ, \quad \phi = 0^\circ$

Figure 1. Room Temperature Spectra of X-Ray Damaged Crystals of Commercial and Purified Strontium Acetate.

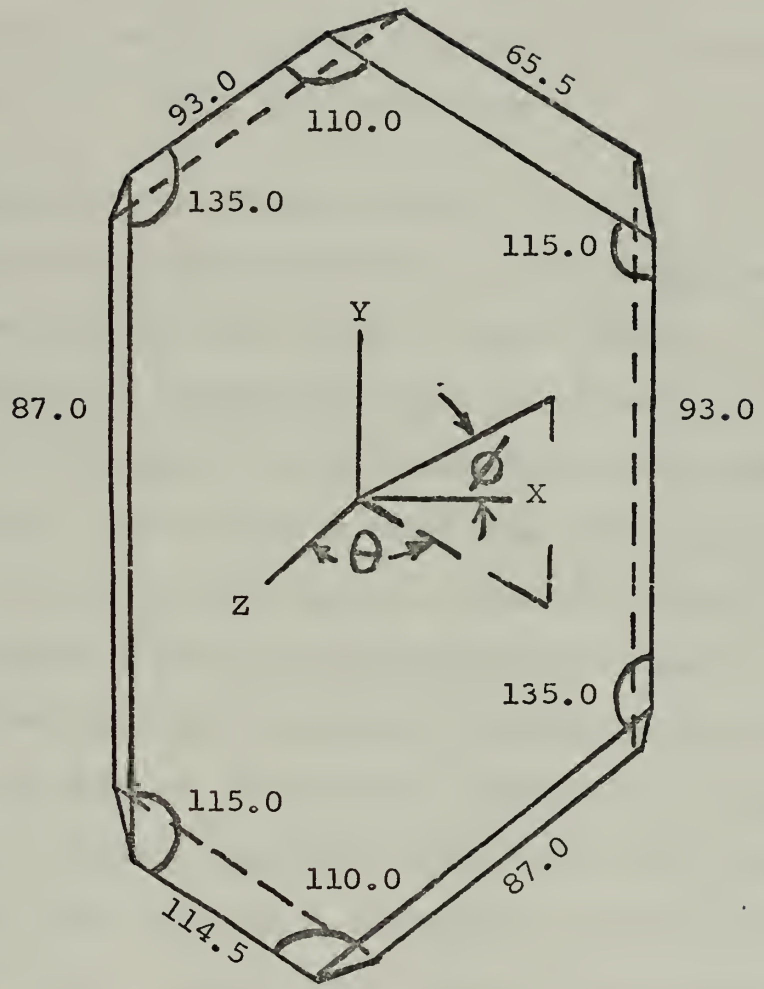


Figure 2. A Single Crystal of $Sr(CH_3CO_2)_2 \cdot \frac{1}{2} H_2O$ showing the angles between the edges and faces of the Crystal, and the Orthogonal Crystal Axis System.

of the crystal on the rod determined the angle in the ϕ direction. The quartz rod itself was positioned within the cavity by attaching the rod to an aluminum shaft by means of a clip. The shaft was connected to a pointer which indicated the angles in the θ direction. It is estimated that the angular position of the crystal in the cavity is known to within ± 1° using this procedure.

C. PROCEDURES FOR TAKING SPECTRA

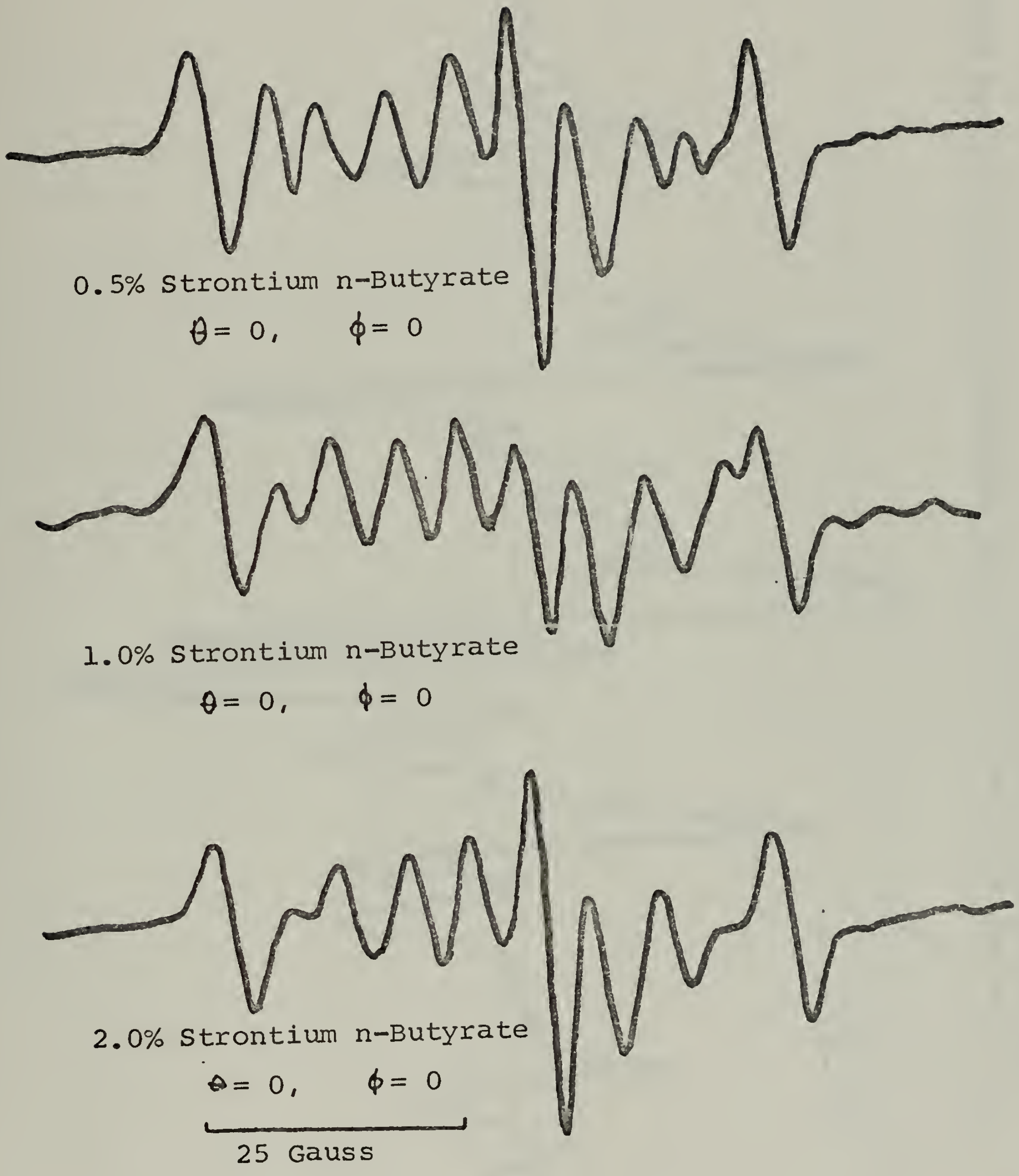
The crystals were exposed to x-ray radiation at 45 kV and 40 mA for one hour using a copper target. The crystals were mounted on transparent tape and placed in the open windows of the ports. All irradiations were made at room temperature. The crystals were then positioned on the quartz rod as described above. EPR spectra were then taken with a Varian V-4502-06 X-band EPR spectrometer using 100 kHz modulation. Spectra used to obtain damage ratios were obtained within one hour after irradiation. Spectra used to obtain coupling constants were taken from crystals about two weeks after they were irradiated. The acetate lines decay much more rapidly than those of the impurity during this period and this makes assignment of the splittings much easier. Spectra used to obtain coupling constants were taken at each 30° interval in both the θ and ϕ direction.

V. RESULTS

A. SPECTRA OBSERVED

Sample spectra of x-ray damaged single crystals of strontium acetate hemihydrate doped with various concentrations of strontium n-butyrate are given in Fig. 3. These spectra may be compared with that of undoped x-ray damaged strontium acetate given in Fig. 1. All of these spectra were obtained within one hour after irradiation at room temperature. A distinguishing characteristic of the n-butyrate doped strontium acetate spectra is the relative amplitude of the second and third lines in from the wings. The second line becomes less prominent with increasing concentrations of strontium n-butyrate. The second line was found to be from the acetate radical by direct comparison of these spectra with that of strontium acetate.

The spectrum of strontium isobutyrate doped strontium acetate is shown in Fig. 4. This spectrum was taken shortly after irradiation. The spectrum shown in Fig. 5 was taken approximately two weeks later where the only species remaining was the isobutyrate radical. No anisotropy could be found for this radical. The spectrum can be easily interpreted as due to six equivalent protons. The relative intensities are 1:6:15:20:15:6:1 and the radical must be $(CH_3)_2\dot{C}COO^-$.



0.5% Strontium n-Butyrate
$\theta = 0, \quad \phi = 0$

1.0% Strontium n-Butyrate
$\theta = 0, \quad \phi = 0$

2.0% Strontium n-Butyrate
$\theta = 0, \quad \phi = 0$

Figure 3. Room Temperature Spectra of X-Ray Damaged Strontium Acetate Doped with Various Amounts of Strontium n-Butyrate.

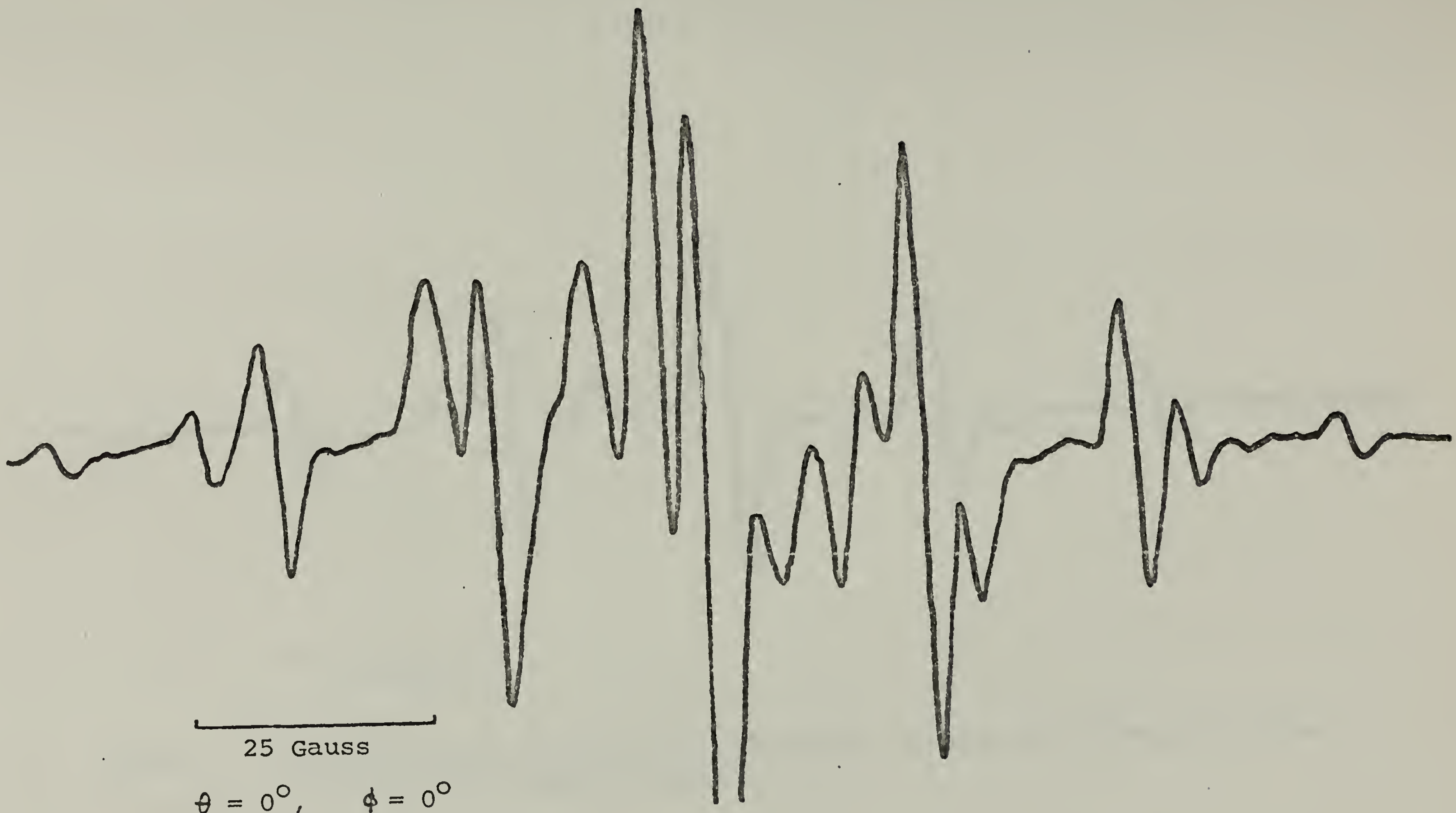


Figure 4. Room Temperature Spectrum of X-Ray Damaged Strontium Acetate Doped with Strontium Isobutyrate.

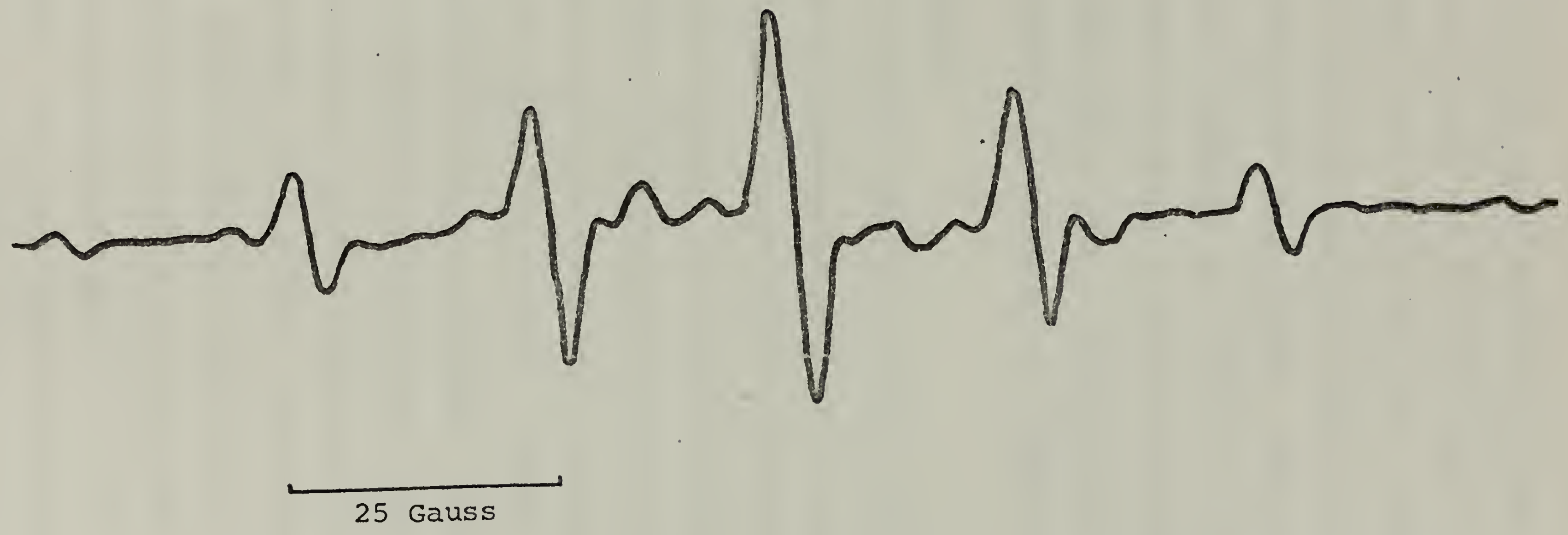


Figure 5. Room Temperature Spectrum of Strontium Isobutyrate Remaining After Decay of the Acetate Radical.

B. DATA

Coupling constants were measured at each orientation. Since readings were made at 30° intervals in both the θ and ϕ directions for 180° there were a total of 42 data points for each coupling constant used in the computations. However, only 32 points were unique. These experimentally obtained coupling constants are listed in Table 1. The angular dependence of these coupling constants is shown in Fig. 6. The data points may be compared with the curves obtained by refining the data by the method of least squares.

C. DATA REDUCTION

A computer program written by Tolles [14] was used to obtain the best coupling constants by the method of least squares and compute the principal values and their associated direction cosines. The direction cosines were computed with respect to the assigned crystal axis. This program requires that the approximate principal values and the rotations necessary to place the crystal axis upon these values be provided as input parameters. These parameters can be easily obtained by plotting the experimental coupling constants on a sterographic projection at the position indicated by the crystal orientation. A point near the high value and another near the low value of the coupling constants are picked such that they are 90° apart. Another point is picked such that it is 90° from both of these two points. This will give an estimate of the intermediate principal value. These three points are then

		AH_1 (MHz)	AH_2 (MHz)	AH_3 (MHz)
0	0	59.4	45.7	29.0
20			44.9	
30		43.1		24.8
60		38.4	37.6	25.2
90		60.7	39.3	26.9
120		73.9	41.4	30.8
150		75.2	43.6	31.6
180		59.8	45.7	28.6
0	30	60.7	46.1	29.5
30		43.6	42.3	26.5
60		40.2	40.2	22.6
90		58.9	37.2	25.6
120		68.3	42.3	28.2
150		71.8	45.3	29.9
180		61.1	46.6	29.5
0	60	59.4	46.6	29.5
30		47.4	47.0	25.6
60		43.1	42.7	23.1
90		53.4		23.9
120		65.8	41.9	25.6
150		66.2	42.7	27.8
180		60.2	47.4	29.5

Table 1. Coupling constants and magnetic field orientations.

Table 1 (Continued).

		AH_1 (MHz)	AH_2 (MHz)	AH_3 (MHz)
0	90	60.2	47.4	29.5
30		59.8	45.3	27.8
60		53.8	42.3	25.6
90		48.3	36.7	24.8
120		50.4	38.0	25.6
150		57.2	42.7	27.3
180		60.2	47.0	29.5
0	120	59.8	47.0	29.5
30		66.2	44.9	30.3
60		65.8	41.9	28.2
90		51.3	36.7	25.6
120		47.0	31.2	23.9
150		44.4	44.0	26.1
180		60.2	47.0	29.9
0	150	60.7	46.6	29.5
30		73.0	44.9	31.2
60		70.9	41.9	29.9
90		55.1	38.0	26.9
120		39.7	27.8	26.1
150		44.9	38.0	25.6
180		60.2	47.0	29.5

Table 1. Coupling constants and magnetic field orientations.

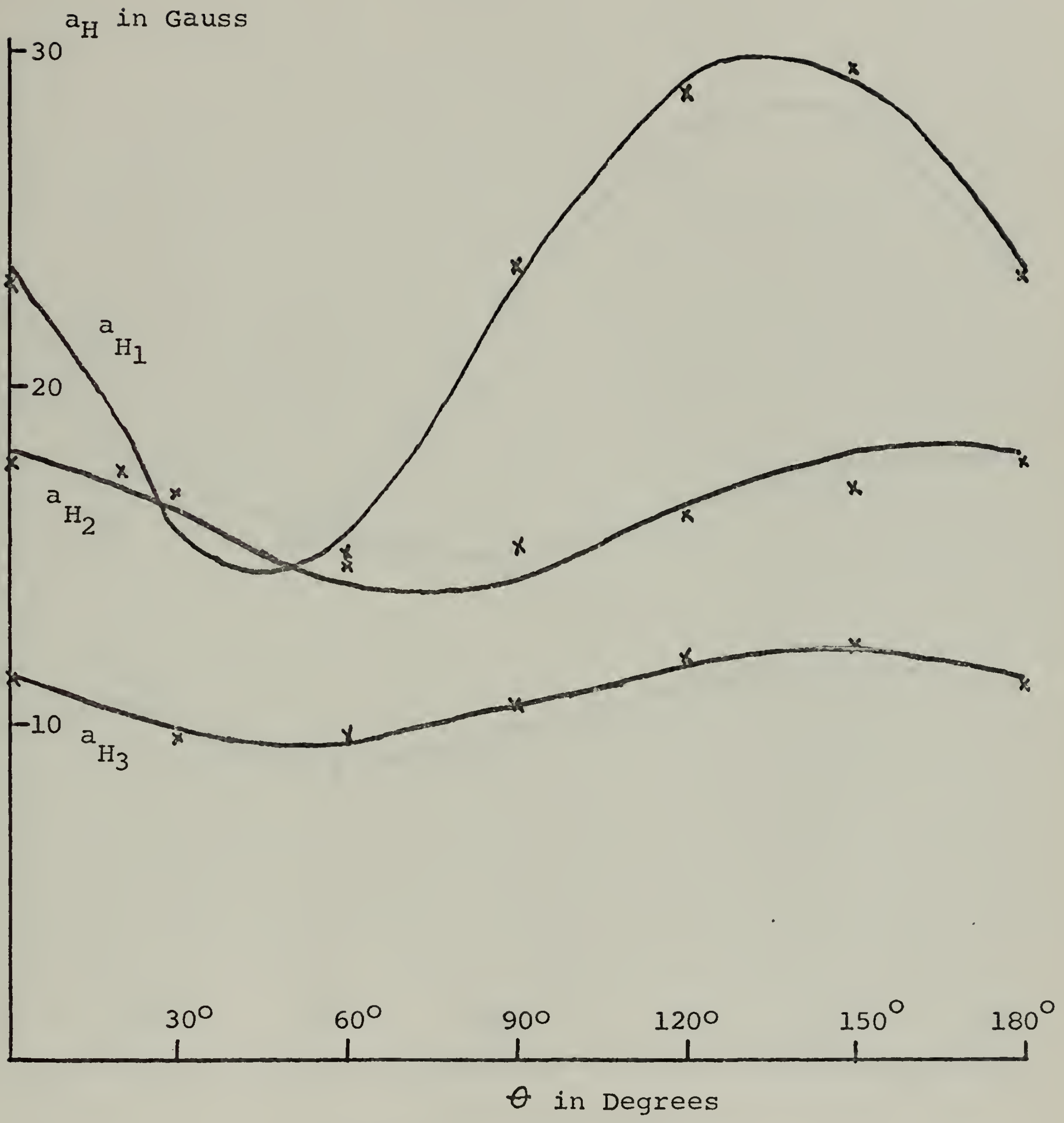


Figure 6A. Coupling constants of room temperature n-Butyrate radicals as a function of the orientation of the magnetic field $\phi = 0°$.

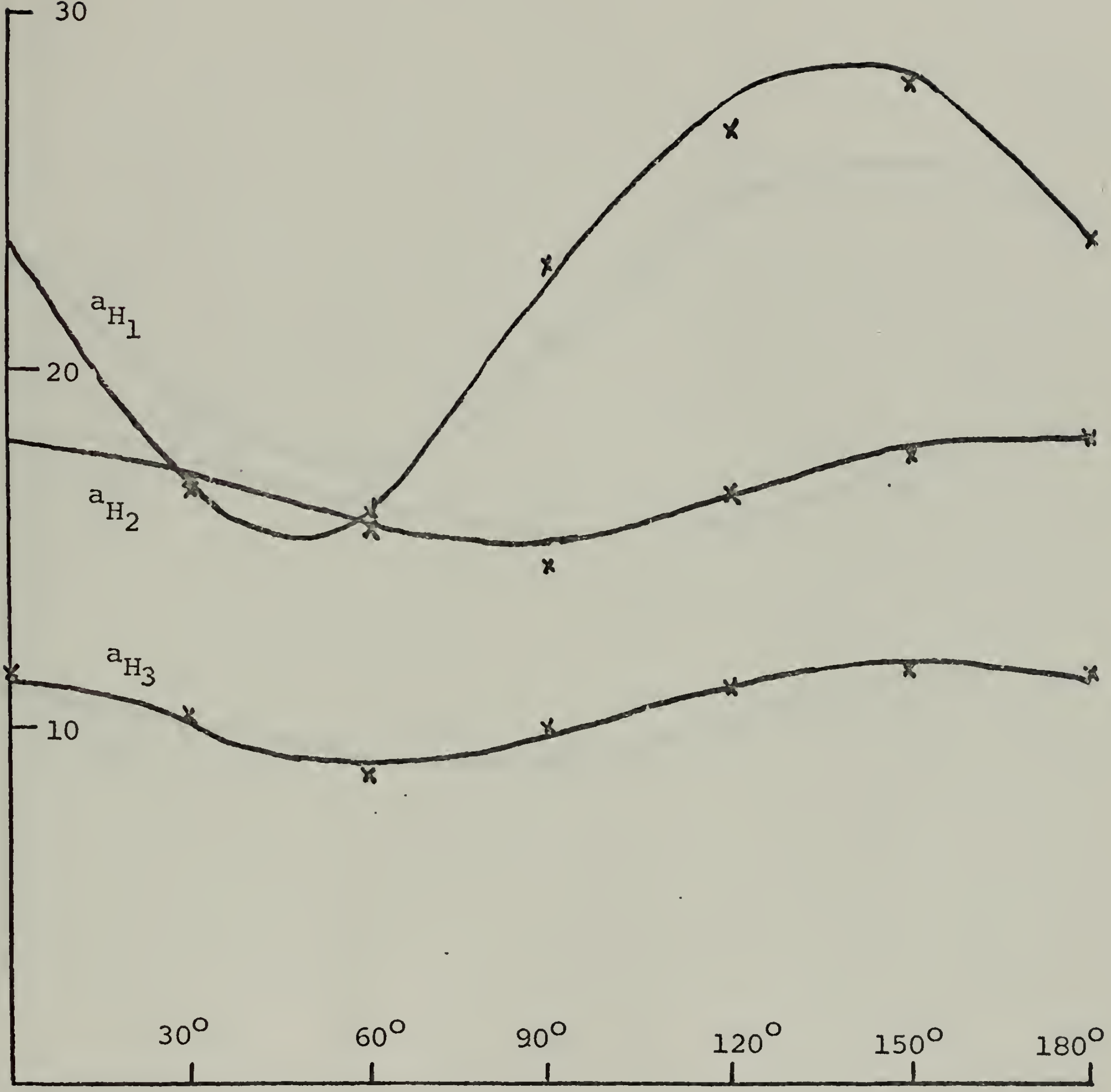


Figure 6B. $\phi = 30^{\circ}$

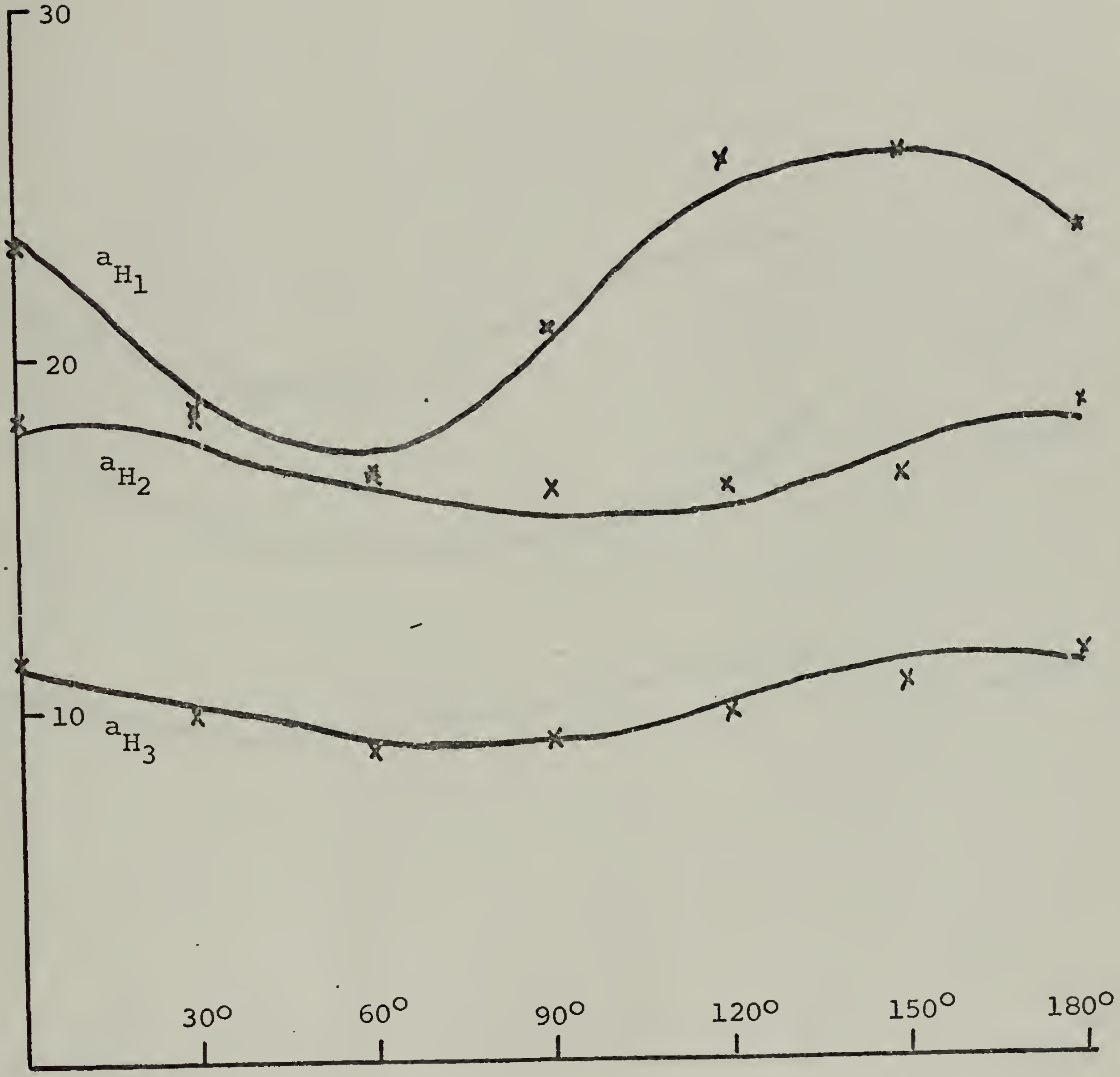


Figure 6C. $\phi = 60^{\circ}$

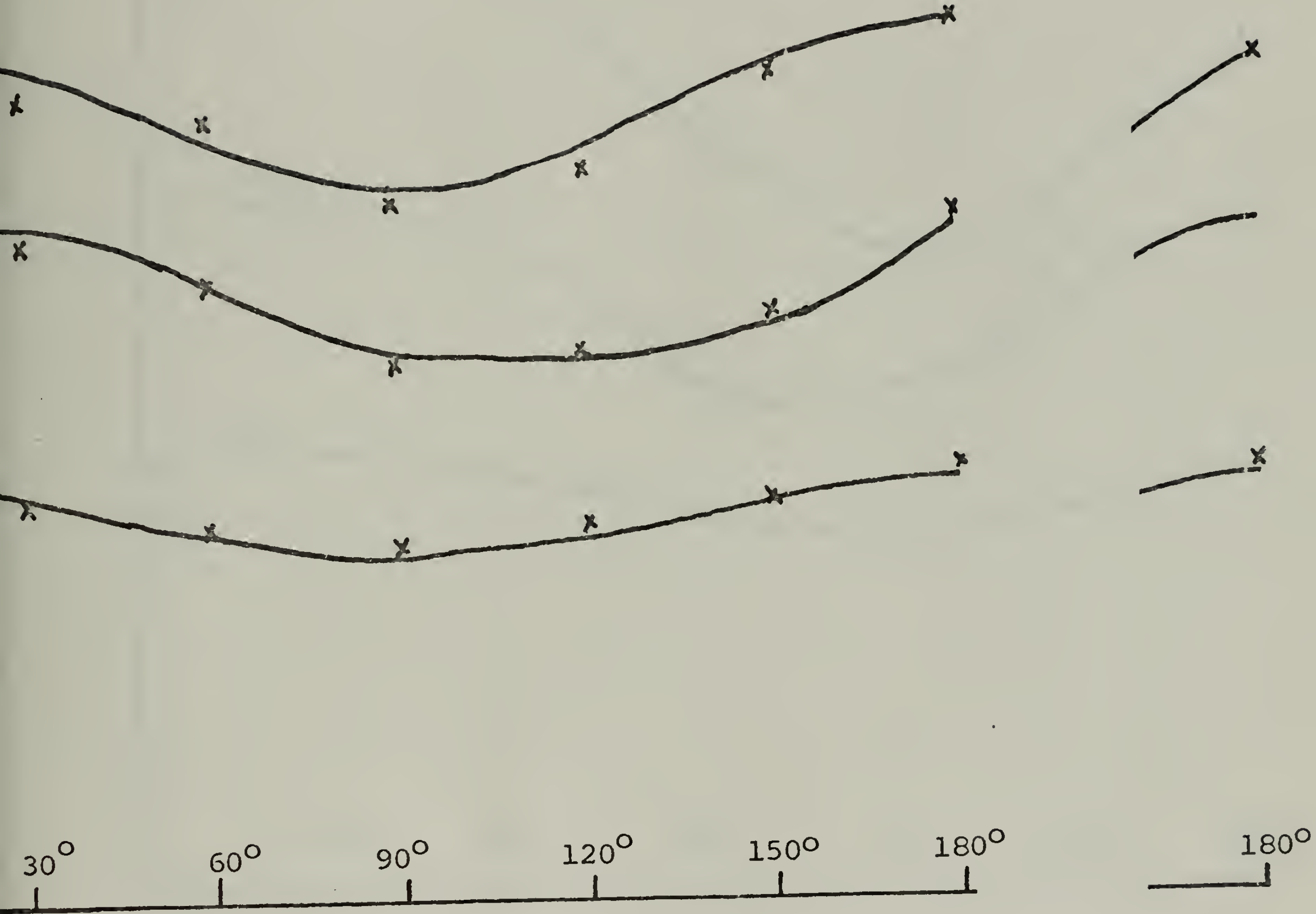


Figure 6D. $\phi = 90^{\circ}$

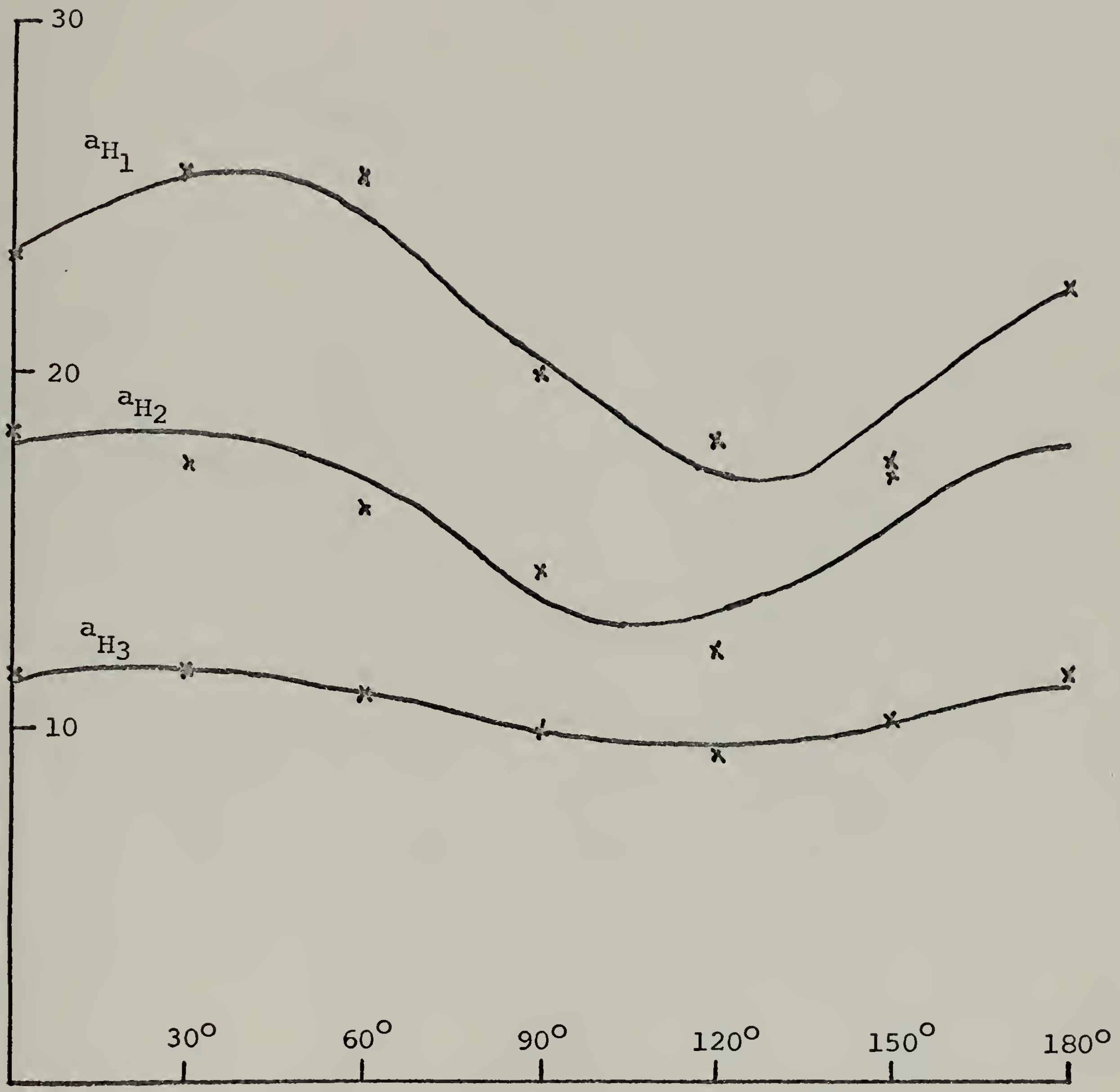


Figure 6E. $\phi = 120^\circ$

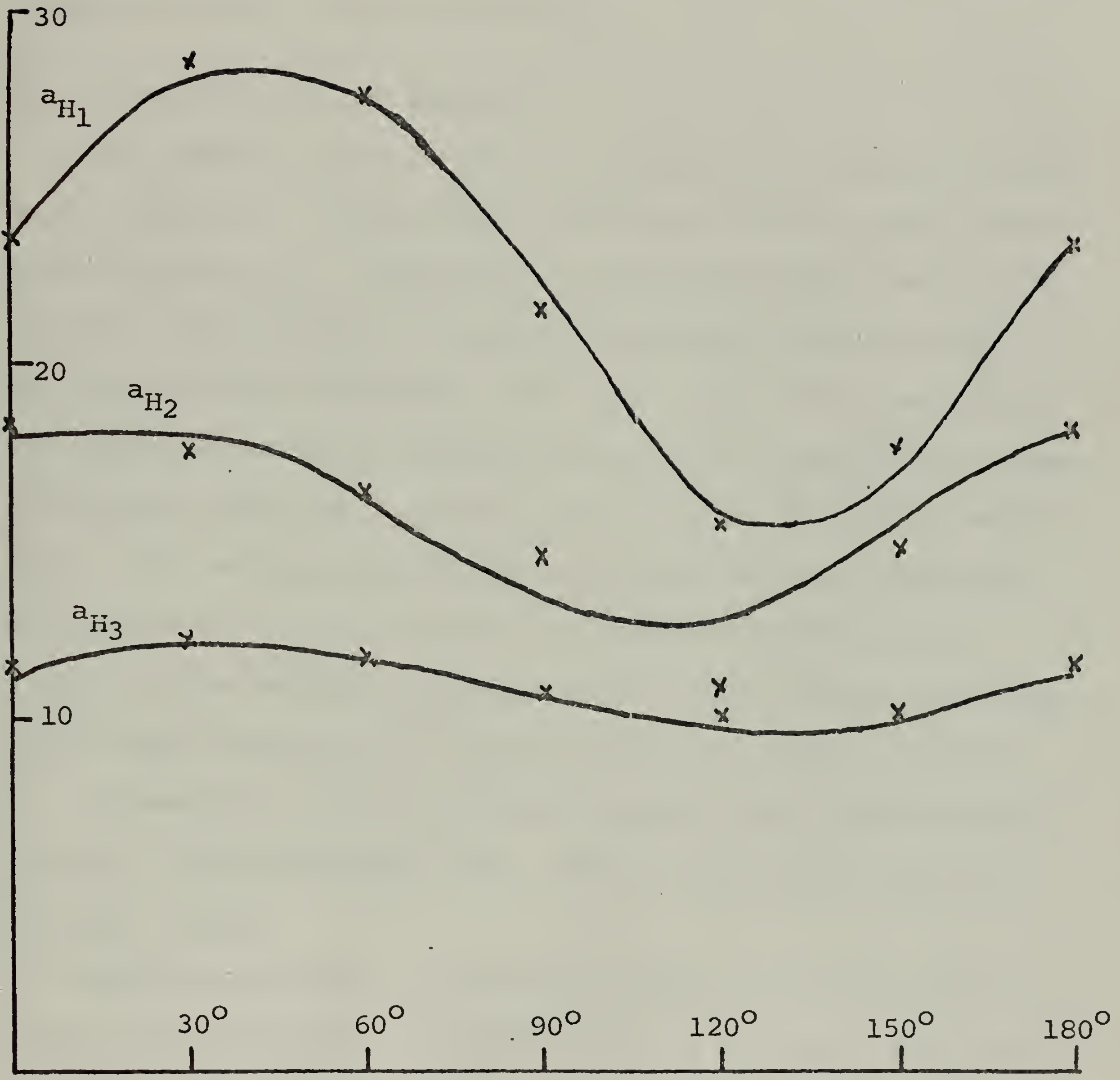


Figure 6F. $\phi = 150^\circ$

rotated until each lies upon one of the axes of the sterographic projection. The reverse of these rotations are the required rotation parameters. The results of this computation are given in Table 2.

D. INTERPRETATION OF RESULTS

The spectra shown in Fig. 3 consists of 8 lines of near equal intensity. These eight lines are due to three inequivalent hydrogens. The radical giving this spectrum has the formula $CH_3CH_2\overset{\circ}{C}HCO_2^-$. The splittings are shown in Fig. 7. The top spectrum is at the $\theta = 0^\circ$, $\phi = 0^\circ$ orientation. At other orientations the splitting is not always so obvious. The bottom spectrum is at the $\theta = 30^\circ$, $\phi = 0^\circ$ orientation. The assumed splittings are shown over the spectra. The spectra are distorted by the residual spectra from radicals from acetate, propionate and other unknown species. Heller and McConnell [6] x-ray irradiated single crystals of β-succinic acid, a similar species, and obtained the radical $HOOCCH_2\dot{C}HCOOH$. This radical also had a spectrum of eight lines.

Tolles and others [1] have determined the principal values and direction cosines for both the acetate and propionate radical in strontium acetate. Their results are reproduced in Table 3. Comparing the anisotropic principal values and direction cosines obtained for the n-butyrate radical reveals a distinct similarity. Both the n-butyrate and the propionate radicals must be oriented very nearly the same way in the crystal. Further comparison with the values

Species	Principal Values (MHz)	Direction cosines x	y	z
$CH_3-CH_2-\dot{C}H-CO_2^-$				
H_1	-83.59 ± 0.61	0.701	0.000	-0.714
	-54.22 ± 0.85	0.013	0.999	0.013
	-39.44 ± 0.88	0.713	-0.018	0.700
H_2	51.89 ± 0.52	0.222	-0.214	-0.951
	43.65 ± 1.04	0.668	0.744	-0.012
	35.59 ± 1.00	0.710	-0.633	0.309
H_3	34.28 ± 0.22	0.594	-0.137	-0.792
	27.28 ± 0.29	-0.617	0.554	-0.559
	25.17 ± 0.31	0.515	0.821	0.225

H_1	H_2	H_3
$-1.1^\circ \pm 3.1^\circ$	$2.2^\circ \pm 15.0^\circ$	$66.3^\circ \pm 6.6^\circ$
$-45.5^\circ \pm 0.6^\circ$	$-72.0^\circ \pm 2.3^\circ$	$-52.4^\circ \pm 1.4^\circ$
$-0.3^\circ \pm 1.7^\circ$	$44.0^\circ \pm 14.0^\circ$	$13.0^\circ \pm 2.4^\circ$

Table 2. Coupling tensors observed in irradiated n-butyrate doped strontium acetate.

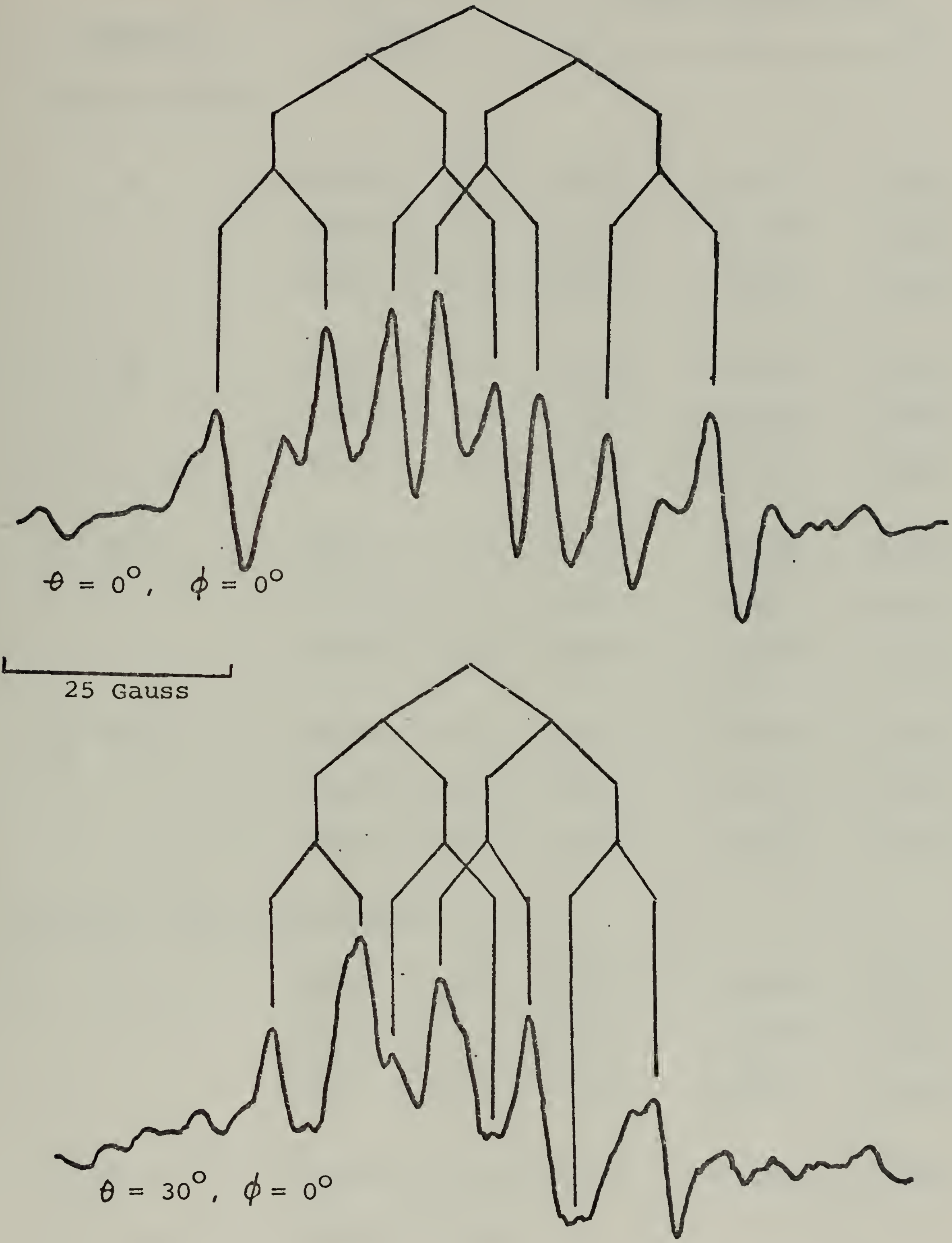


Figure 7. Examples of splitting assignments made to sample spectra of strontium n-Butyrate.

	Principal Values	Direction cosines		
Species	(MHz)	x	y	z
$\cdot CH_2CO_2^-$ (233°K)				
H_1	-90.94 ± 0.3	0.986	-0.157	0.055
	-58.57 ± 0.4	0.157	0.988	0.006
	-29.24 ± 0.4	-0.055	0.002	0.998
H_2	-91.47 ± 0.3	0.519	-0.088	-0.850
	-55.05 ± 0.4	0.187	0.982	0.013
	-31.37 ± 0.6	0.834	-0.166	0.527
H_1'	-88.40 ± 0.4	0.444	0.485	-0.753
	-57.88 ± 0.5	0.733	-0.680	-0.007
	-30.62 ± 0.6	0.516	0.549	0.658
H_2'	-90.64 ± 0.3	0.201	0.237	0.951
	-56.66 ± 0.5	0.740	-0.673	0.011
	-31.31 ± 0.9	0.642	0.701	-0.310
$CH_3\dot{C}HCO_2^-$ (room temperature)				
a_H	-86.6 ± 0.8	0.676	0.098	-0.730
	-54.1 ± 1.2	0.085	0.974	0.209
	-31.3 ± 1.9	0.732	-0.203	0.650
a_{CH_3} a	74.78 ± 0.14	-0.373	-0.220	0.901
a_1	67.64 ± 0.10			

Table 3. Coupling tensors observed in irradiated strontium acetate. (From Tolles, Sanders, and Gisch [1])

for the acetate radical reveal that there is only one magnetically distinct site, H_2, for the n-butyrate radical. This means that, in common with the propionate radical only one of the two available acetate sites is occupied by the n-butyrate radical and that within this site only one of two possible rotamers is thermally populated. This is further evidence that the acetate ions are not related by symmetry in this crystal.

The isotropic principal values permit the determination of the angle between the CH bond on the β carbon and the symmetry axis of the π electron orbital by use of McConnell's [6] formula

$$A(\text{isotropic part}) = B_o + B\cos^2\theta .$$

In this formula θ is the angle between the symmetry axis of the π electron orbital and the projection of the CH bond. The constants used here are those reported by Wells and Box [10] . These values are $B_o = 3.2$ MHz and $B = 123.3$ MHz. Applying these constants and the experimentally determined principal values the results are:

Proton 1: = ± 62.8°

Proton 2: = ± 55.0°

A graphical representation of the orientation of the hydrogen atoms on the β carbon is given in Fig. 8. The view presented is that along the carbon bond. Wells [15] applied the same values for the constants B_o and B to

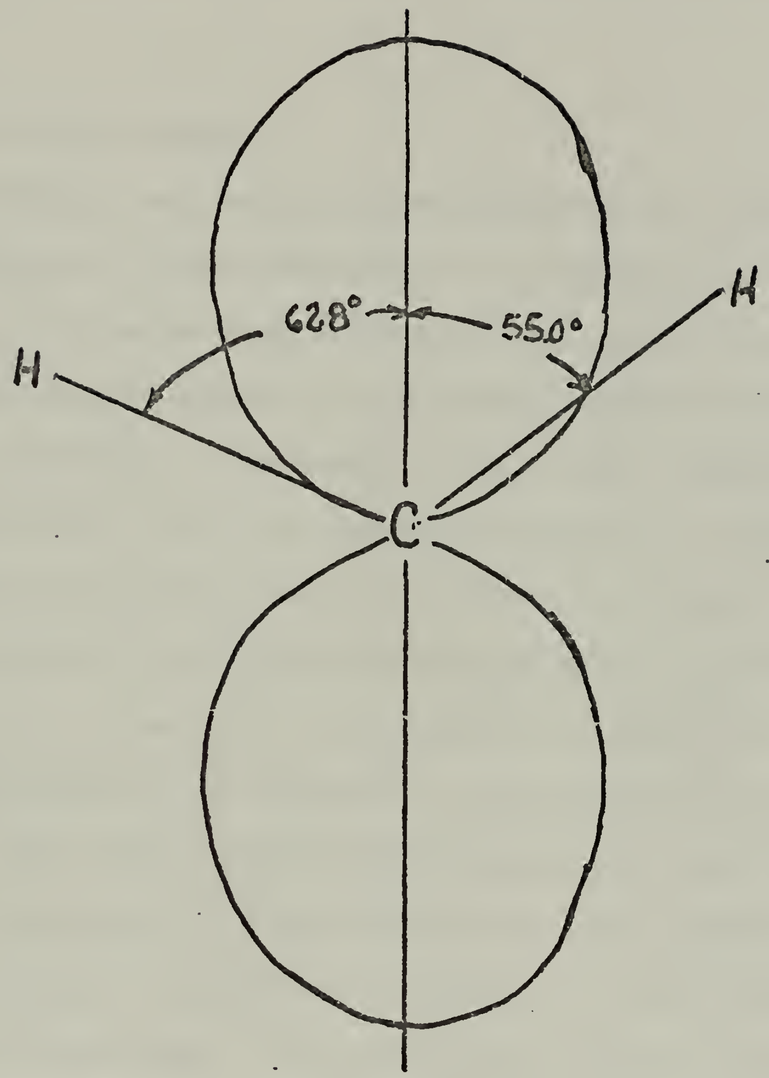


Figure 8. Orientation of the β Carbon Hydrogens.

succinic acid and obtained dihedral angles of 39° and 66°. The n-butyrate chain then must be twisted from its preferred position in order to fit in the strontium acetate crystal lattice.

E. SELECTIVITY RATIOS

Selectivity ratios have been obtained for both n-butyrate and isobutyrate doping material in strontium acetate crystals. The selectivity ratio is the slope of the ratio of damaged doping material to acetate versus concentration of doping material. The ratio is 300 with isobutyrate doping and about 500 with n-butyrate doping. The selectivity ratio for isobutyrate is presented in Fig. 9. Tolles has reported the ratio for propionate and it is also shown. The ratio for n-butyrate is presented in Fig. 10.

Computation of the ratio for isobutyrate was straightforward. The amplitude of the isobutyrate line with a relative intensity of 6 was measured. This was multiplied by 64/6 to give the relative intensity of the entire isobutyrate spectrum. The sum of the relative intensities for isobutyrate is 64. The amplitude of one of the outer acetate lines was measured and then multiplied by 8. The acetate spectrum consists of two groups of lines with each group having a relative intensity of 1:2:1. The total relative intensity, therefore, is 8. The ratio of these two numbers gives the isobutyrate to acetate damage ratio. The isobutyrate concentration was known from the amount of doping material added to a known amount of strontium acetate.

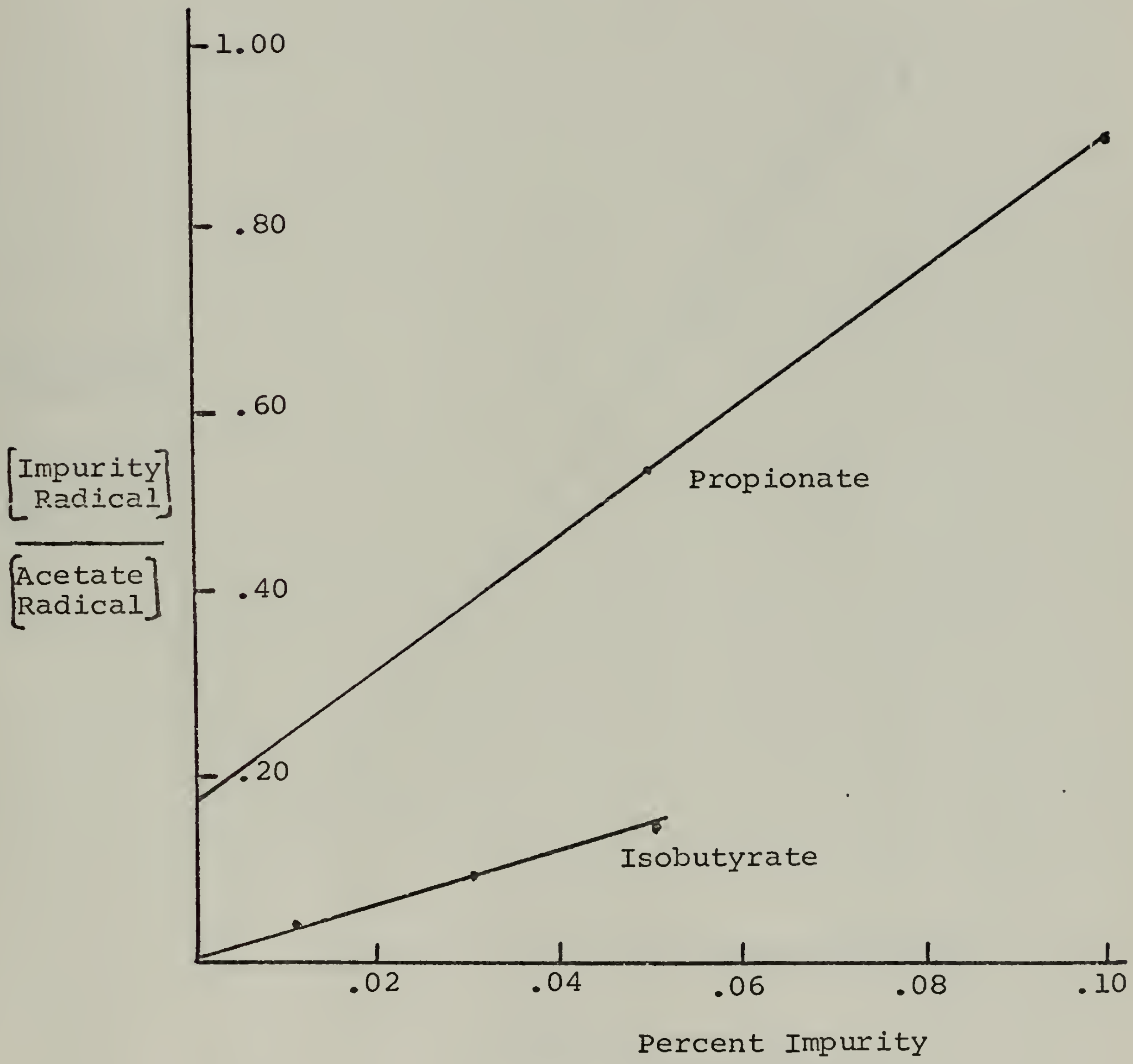


Figure 9. Selectivity ratios of propionate and isobutyrate in stontium acetate.

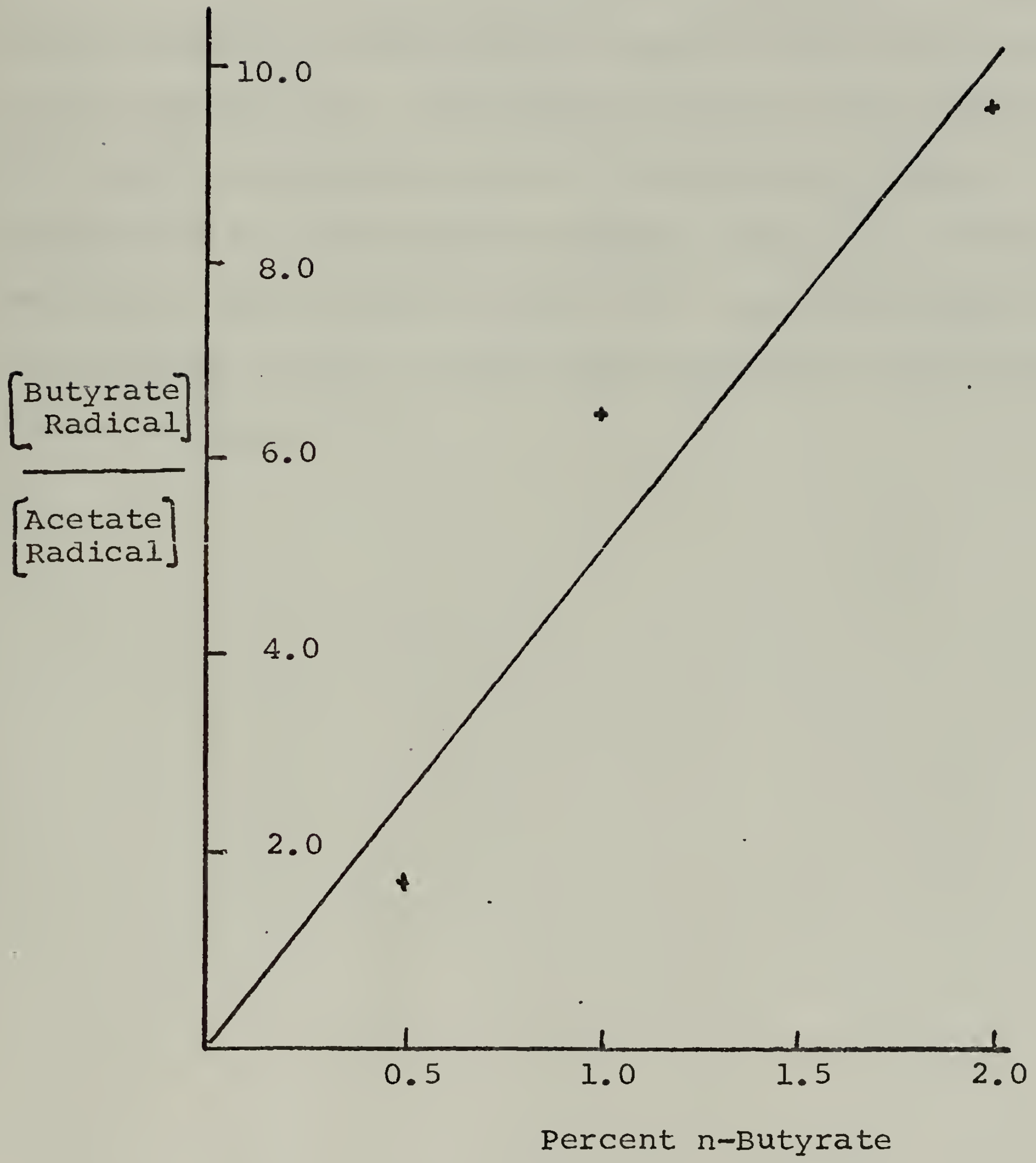
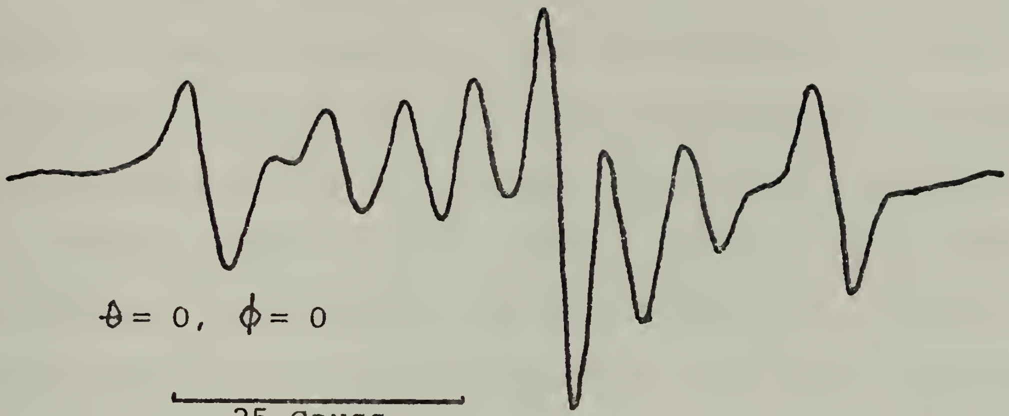
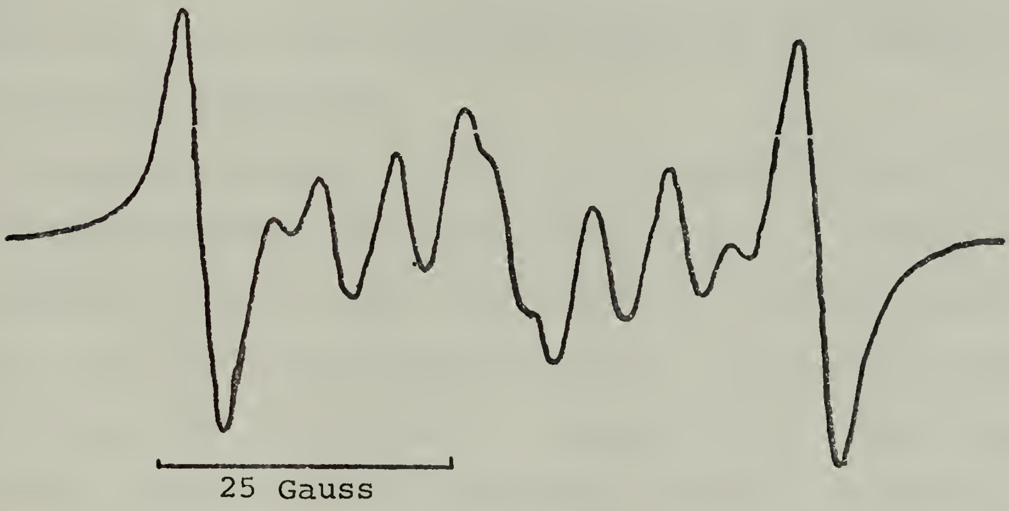


Figure 10. Selectivity Ratio of n-Butyrate in Strontium Acetate.

The selectivity ratio for n-butyrate cannot be found so easily. The lines are close together and they will ride up one another making amplitude measurements hazardous. The spectrum was simulated using a computer program written by Tolles [16] . The intensity parameters were varied until a spectrum resembling a spectrum with known concentrations was obtained. The damage ratio was then computed from the known intensities used in the computer program. A comparison of the computer simulate spectrum with that of an actual one is given in Fig. 11. Some information on isobutyrate in zinc acetate would indicate a selectivity ratio of about 8 to 1.



Actual Spectrum of n-Butyrate in Strontium Acetate



Computer Simulated Spectrum

Figure 11. Comparison of Computer Simulated Spectrum with Actual Spectrum.

VI. SUMMARY

Strontium acetate has proved to be a suitable host in which to study a number of radical fragments. So far propionate, isobutyrate and n-butyrate have been studied. The ultimate number of materials that may be introduced is, of course, unknown. Other likely candidates are adipate and succinate. It would also be interesting to try some of the amino acids. It is an unusual fact, that for both propionate and n-butyrate in strontium acetate crystals, that only one of the two acetate sites is occupied by damaged ions and that within this site, only one rotamer of the damaged ion is thermally populated.

Strontium acetate, if it is to be used as a host crystal for other materials, must be extremely pure. Commercial strontium or acetic acid, from which the acetate may be made, that is usually available in the laboratory is not pure enough for this purpose. Distillation of the acetic acid has proved to be an acceptable method to produce a product of the required purity. It is possible to produce acetic acid with a propionate content of 0.0001% or less.

Selectivity ratios for n-butyrate and isobutyrate ion damage in strontium acetate crystals have been found. The ratio for n-butyrate is about 500 to 1 and the ratio for isobutyrate is 300 to 1. Tolles, Sanders and Gisch [1] first reported this phenomenon for propionate in strontium

acetate crystals. The selectivity ratio they reported was 700 to 1. Large selectivity ratios have now been shown to be general for organic acid anions. The mechanism for delocalization of the damage and the resulting large selectivity ratios remains unknown.

The unpaired electron in the n-butyrate radical has been shown to be in a p orbital of the α-carbon when x-ray irradiated at room temperature. Additional information on the potential holes in the strontium acetate crystalline structure has been provided.

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13. ABSTRACT

An EPR study of x-ray irradiated isobutyrate and n-butyrate doped strontium acetate hemihydrate has been made. The n-butyrate radical exhibited anistropy while the isobutyrate did not. The n-butyrate radical ion has a spectrum of 8 lines of equal intensity. The unpaired electron is on the α carbon and the two β carbon hydrogens are inequivalent. The n-butyrate radical has been shown to be oriented in very nearly the same position as the propionate radical previously reported and it occupies only one of the two acetate sites. Within this site only one rotamer of the damaged ion is thermally populated. The isobutyrate ion is selectively damaged by a ratio of 300 to 1, and the ratio for n-butyrate is about 500 to 1.

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ESR						
Acetates						
Isobutyrates						
n-Butyrates						
Strontium Acetate						
Strontium Isobutyrate						
Strontium n-Butyrate						
Zinc Acetate						
Zinc Isobutyrate						

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